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STUDY ON ITO THIN FILMS PREPARED BY MULTI-ANNEALING TECHNIQUE

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ABSTRACT

Indium tin oxide (ITO) thin films have been successfully prepared by a solution process followed by a multi-annealing method. In this study, we focus on the use of multi-annealing method, for which each layer was annealed at a suitable temperature, instead of a conventional annealing way, by means of a rapid thermal annealing system, in order to improve the film quality. The crystalline structure and surface morphology of the ITO thin films were investigated by using X-ray diffraction (XRD) spectrometer, atomic force microscope (AFM) and scanning electron microscope (SEM). It has been obtained that all of ITO films exhibit a single phase with (222)- and (440)-preferred orientations. The AFM and SEM observations show that the particle size of ITO films was about 10 nm and the ITO film thickness was 180 nm, respectively. In sequence, the electrical properties of ITO thin films were evaluated by using four-point probe and Hall effect measurement methods, and the optical properties were investigated by UV/VIS spectrometer. The results show that the best ITO films have electrical resistivity of 2.6×10^{-3} Ω.cm and transparency higher than 90 %, which strongly supports to the application of electrode in solar cell, LED or transistor devices from viewpoints of low-cost production and low-energy consumption.

Keywords: ITO, transistor, TCO electrode, solar cell, LED.

1. INTRODUCTION

Transparent conducting oxide (TCO) thin films have been extensively studied because of their high electrical conductivity and optical transparency. They are used in photo electronic devices such as solar cell, flat panel display, and organic light emitting diode. As known as a typical TCO thin film, indium tin oxide (ITO) is a wide gap semiconductor with a relatively low resistivity, and extensively used as a transparent material in the visible spectrum range [1 - 5]. In general, ITO thin films have been fabricated by various methods such as electron beam evaporation [1], RF magnetron sputtering [2], pulsed-laser deposition [3], spray-pyrolysis [4] and sol-gel method [5 - 9]. Among these methods, the sol-gel route offers some advantages, which are suitable for an ease-to-fabricate process, because it is low-cost, quick, and rarely affected by environmental factors. However, we found that the ITO thin films fabricated by sol-gel technique using conventional annealing easily get a strongly cracked surface. Hence, in this work, we have also prepared ITO thin films by sol-gel technique, but using multi-annealing method, instead of the conventional one, to expect that their quality can be improved without any cracks.

2. EXPERIMETAL METHODS

First, SiO_2/Si substrates with 10 × 10 mm^2 in plane dimensions were cleaned and dried in acetone and fresh air blower, respectively. Second, the SiO_2/Si substrates were dropped with 10%-tin-doped indium oxide precursor onto their surface, and then rotated with speed of 2000 rpm. Third, the samples were hot-dried in air at 150 ^oC for 1 min, and dried at 250 ^oC for 5 min. Finally, the ITO thin film samples were annealed by using multi-annealing technique, of which each layer was crystallized at a suitable temperature using a rapid thermal annealing (RTA) furnace before covering a next layer. The process above was repeated to obtain the desired thickness of the ITO thin film layers. In order to investigate the effect of annealing temperatures on the quality of ITO thin films, the samples were treated at various temperatures such as 500, 550 and 600 ^oC in the mixture of $O_2 : N_2$ gases ratio of 1 : 4. For each temperature, the annealing time is 10 min.

The crystallization and the orientation of the ITO thin films were analyzed by X-ray diffractometer (XRD, Bruker D5005) at room temperature, using the Cu-Kα radiation with wavelength λ = 1.5405 Å, and the incident angles 2θ in the range of 10° to 70° with the step of 0.03°. The morphological property of the ITO thin films was observed by using scanning electron microscopy (Nova NANOSEM 450) and atomic force microscope (AFM XE 100 Park System). The electrical properties of ITO thin films were investigated by a four-point probe technique and Hall effects measurement method at room temperature. The transmittance of ITO thin film was measured by UV/VIS spectrophotometer, for which the ITO thin film was deposited on a quartz substrate at 600 ^oC.

3. RESULTS AND DISCUSSION

Figure 1 shows the crystal structure analysis of the ITO thin films. The results exhibit a clear polycrystalline behavior with (222) and (440) orientations of ITO thin films. In this experiment, the annealing temperatures were not found to cause a considerable change in the stoichiometric structure of ITO thin films, when investigating from 500 to 600 °C, from a viewpoint of XRD measurement.

Figure 2 shows SEM surface micrographs of the ITO thin films annealed at (a) 500 ^oC, (b) 550 ^oC and (c) 600 ^oC. One can observe that the surface morphology of all ITO thin films is uniform and seems to be formed by small nano-sized grains. Also, we can see that the grain size is increased with increasing the annealing temperature, that is, the crystalline quality of the ITO thin film becomes better when the annealing temperature is increased. In fact, we estimate that the grain size of the sample annealed at 550 ^oC is about 12 nm.

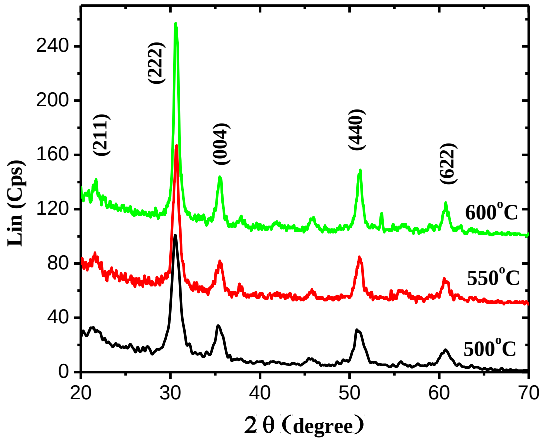

Figure 1. XRD patterns of ITO thin films annealed at 500 ^{o}C, 550 ^{o}C and 600 ^{o}C.

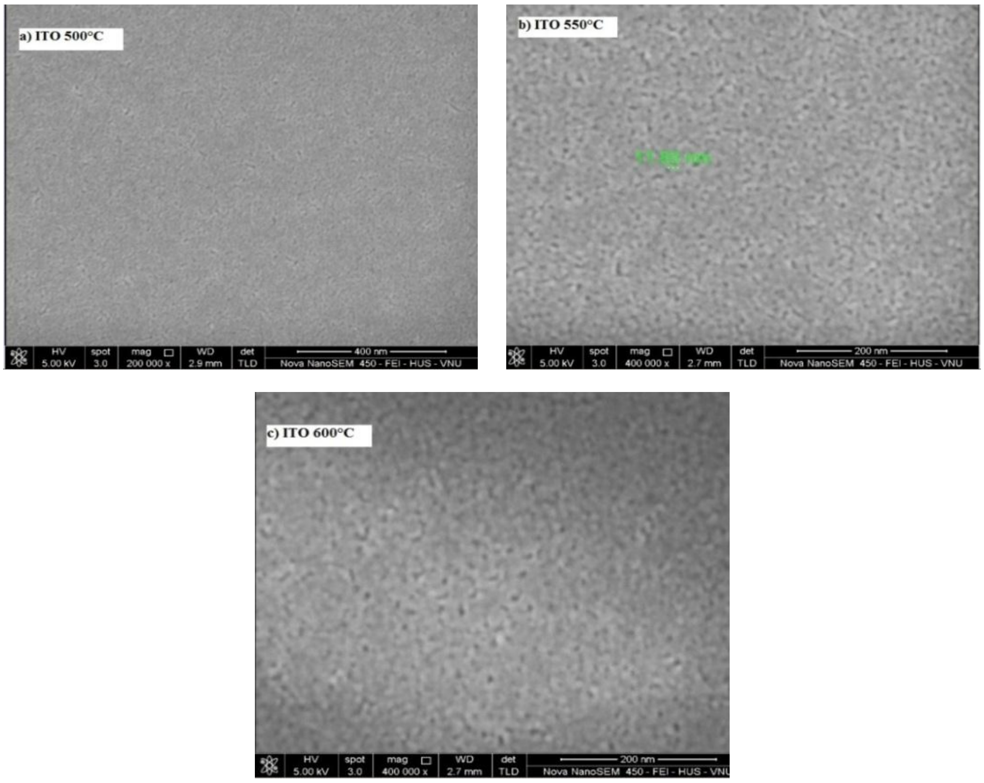

Figure 2. SEM surface micrographs of the ITO thin films annealed at (a) 500 ^{o}C, (b) 550 ^{o}C and (c) 600 ^{o}C.

Beside SEM observation, we also used AFM to investigate the surface roughness of ITO thin films. Figure 3 points out an AFM image of ITO thin film annealed at 600^{o}C. The grain size obtained in Fig. 3 is matched with that observed in Fig. 2 (c). The mean square roughness (Rms) of this sample is about 0.25 nm, which is quite small and comparable with the values reported by other authors [10]. In order to determine the thickness of ITO thin films deposited on SiO_2/Si substrates, the cross-sectional SEM observation was carried out as can be seen from Fig. 4.

According to this figure, the ITO thin films obtained have a typical thickness of 180 nm, and they are well-formed on the SiO_2/Si substrates.

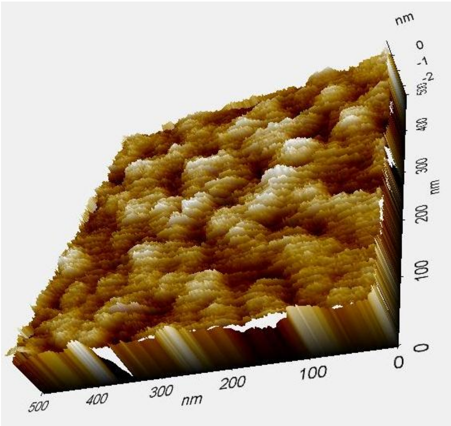

Figure 3. AFM image of ITO thin film annealed at 600 ^oC.

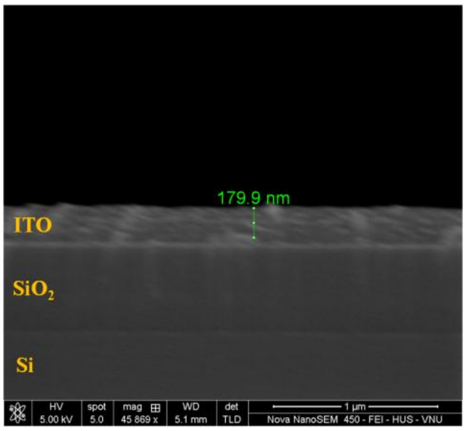

Figure 4. SEM cross-section of ITO thin film.

Table 1 gives electrical properties of the ITO thin films annealed at 500 ^oC, 550 ^oC and 600 ^oC. All samples revealed n-type semiconducting characteristics. When the annealing temperature was increased from 500 ^oC to 600 ^oC, the resistivity decreased from 1.57 × 10^{-2} Ω.cm to 3.02 × 10^{-3} Ω.cm and the Hall electron mobility increased from 1.295 to 3.571 cm^2/Vs. The carrier concentration increased from 3.079 × 10^{20} cm^{-3} to 6.735 × 10^{20} cm^{-3}, if increasing the annealing temperature from 500 to 550 ^oC. However, it then dropped to 5.787 × 10^{20} cm^{-3} at 600 ^oC. From this result, we can extract that the temperature of 600 ^oC is optimum to achieve the highest conductivity, corresponding to the lowest resistivity of 3.02 × 10^{-3} Ω.cm. This value is suitable for electrode application in the TCO devices such as LED, solar cell and transistor memory, even the simple fabrication process is utilized instead of the conventional vacuum process.

Table 1. Electrical properties of the ITO films annealed at 500 ^oC, 550 ^oC and 600 ^oC.

Sample	Annealing Temperature (^oC)	Sheet Resistance R_s (Ω/□)	Resistivity ρ (Ω.cm)	Carrier Concentration (×10^{20} cm^{-3})	Hall Mobility (cm^2/Vs)
A1	500	1700	1.57×10^{-2}	3.079	1.295
A2	550	280	3.33×10^{-3}	6.735	2.658
A3	600	220	3.02×10^{-3}	5.787	3.571

In the total investigation, the best quality ITO thin film in the case of SiO_2/Si substrate was also prepared on a quartz substrate at 600 ^oC, in order to investigate its transmission possibility. Figure 5 shows optical transmittance spectra of the ITO thin film deposited on a quartz substrate. One can be obtained that the transmittance reaches approximately to 90 % in the visible range, if the absorption of the quartz substrate is subtracted. This is actually comparable with the ITO thin film as reported by the other groups [11 - 13].

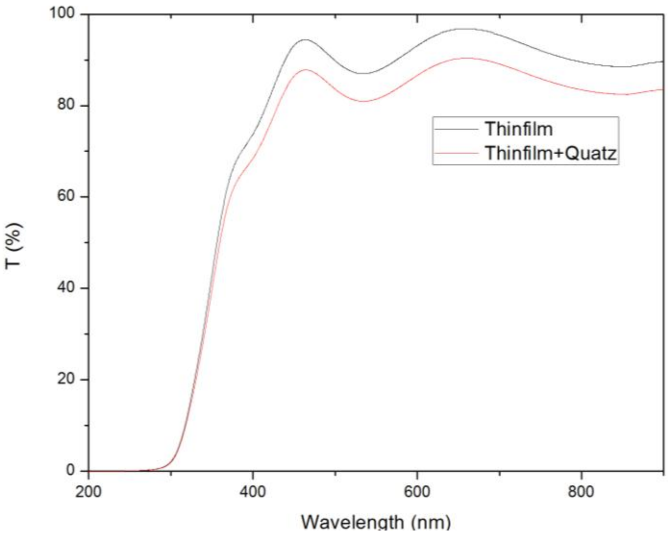

Figure 5. Optical transmittance spectra of ITO thin film annealed at 600 ^{o}C.

From Fig. 5, the band gap of ITO thin film is extracted to be 3.89 eV, and this value is closed to the theoretical and experimental results as reported previously [14]. Generally, the performance of TCO thin films can be quantitatively evaluated by using a parameter named as figure of merit (FOM). The FOM (Φ_H) is expressed through the following equation [15]:

$$\Phi_H = T^{10}/Rs$$

In this formula, T and R_s are corresponded to the transmittance and the sheet resistance of the TCO thin film. Using the equation above, we have calculated that the Φ_H is about 0.158 × $10^{-2}\ \Omega^{-1}$ in our case. Table 2 presents a comparison of ITO thin films quality, in which they were deposited by sputtering or sol-gel technique. One can be seen that the Φ_H of this work is 7.5 times lower than that of the ref. 17, but 2 times higher than that of the ref. 18. Although the Φ_H obtained is still much lower than that obtained from sputtering technique, our process is non-vacuum and less material and low energy consumption.

Table 2. Comparison of ITO thin films quality.

No.	ρ (10^{-4} Ω.cm)	R_s (Ω)	t (nm)	T (%) at 550 nm	Φ_H ($10^{-2}\ \Omega^{-1}$)	Technique	Ref.
1	2.2	22	100	~ 92	1.974	Sputtering	[12]
2	7.2	30	241	~ 90	1.191	Sol-gel	[13]
3	45.9	379	121	~ 88	0.073	Sol-gel	[14]
4	30.2	220	180	~ 90	0.158	Sol-gel	This work

4. CONCLUSIONS

In this work, the 180-nm-thick ITO thin films were successfully fabricated on SiO_2/Si and quartz substrates by a solution-processed method with multi-annealing assistance. Whole ITO thin film samples exhibited a single-phase structure with preferential (222) and (004) orientations. There were not any surface cracks for all cases, and the grain size increased with the increment of annealing temperature. The lowest sheet resistance of ITO thin film annealed at 600 °C was estimated to be 220 Ω/□ with respect to resistivity of 3.02×10^{-3} Ωcm, and the optical transmittance is around 90 % in the visible region of the natural light. As a result, we estimated that the figure of merit is approximately $0.158 \times 10^{-2}\ \Omega^{-1}$. It means that the ITO thin films are suitable to low-cost and simple process, which might bring some promising challenges for application of the TCO electrodes in solar cells, LEDs, transistors or other electronic devices.

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TÓM TẮT

NGHIÊN CỨU CHẾ TẠO MÀNG MỎNG ITO BẰNG PHƯƠNG PHÁP Ủ ĐA LỚP

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Trong nghiên cứu này, màng mỏng ITO được chế tạo bằng phương pháp sol-gel. Tính chất điện, quang và vi cấu trúc của màng mỏng ITO được khảo sát thông qua phương pháp đo bốn mũi dò, máy đo phổ huỳnh quang, máy nhiễu xạ tia X và máy hiển vi điện tử quét. Dựa vào các kết quả phân tích, chúng tôi tập trung vào cải thiện chất lượng của màng mỏng ITO, sử dụng phương pháp ủ đa lớp. Đối với phương pháp này, cứ sau mỗi lần quay phủ thì màng mỏng ITO lại được ủ nhiệt bằng hệ ủ nhiệt nhanh RTA trong khoảng 10 phút, trong hỗn hợp khí O_2 và N_2 theo tỉ lệ 1:4 và nhiệt độ ủ là 500 ^oC, 550 ^oC và 600 ^oC. Màng mỏng ITO thu được có độ dày 180 nm cho thấy điện trở suất khoảng 2.6 x 10^{-3} Ω.cm và hệ số truyền qua của màng ITO đạt giá trị 90 %. Giản đồ nhiễu xạ tia X cho thấy rằng màng mỏng ITO có cấu trúc đa tinh thể với các hạt định hướng theo phương (222) và (440). Các kết quả này cho thấy màng ITO đã chế tạo có thể làm các điện cực trong các ứng dụng cho pin mặt trời, các thiết bị transistor và LED.

Từ khóa: ITO, tran-zi-to, ô-xit bán dẫn, điện cực dẫn trong suốt.